

Atomic-Based Calculations of Two-Detector Doppler- Broadening Spectra

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Abstract

We present a simplified approach for calculating Doppler broadening spectra based purely on atomic calculations. This approach avoids the need for detailed atomic positions, and can provide the characteristic Doppler broadening momentum spectra for any element. We demonstrate the power of this method by comparing theory and experiment for a number of elemental metals and alkali halides. In the alkali halides, the annihilation appears to be entirely with halide electrons.

Keywords: “Doppler Broadening”, “alkali halides”, “momentum density”, enhancement

The coincidence Doppler Broadening method [1-4] provides a powerful probe of the chemical composition of vacancy-related defects in materials. By using two germanium detectors in coincidence, this approach provides spectra into the high momentum region where the momentum density is dominated by atomic-like electrons, thereby providing information about the chemical environment of the positron. This technique has been successfully applied to a wide variety of systems [5-9].

A complete analysis of the resulting spectra requires a well-calibrated set of experimental reference data, or a set of theoretical curves, or both. Reference data are not always readily available, and theoretical calculations are complicated by the fact that existing procedures require full electronic structure calculations on well-defined unit cells [10,11]. Specific atomic configurations are not always available for complicated defect structures and full calculations are expensive for large defects. As a result, interpretation of the spectra is often hampered by an incomplete knowledge of the spectral features associated with the constituent atoms in the sample. In many cases, interpretation of the experimental data does not require a detailed knowledge of the atomic positions; the questions of interest are “Is the positron annihilating with A or B electrons in an AB alloy?” or “Does some element make any contribution to the spectrum?” To answer these questions, we only need to know the general shape of the spectrum associated with each element.

At higher momentum values, greater than around 1 a.u., the spectrum is dominated by contributions from electron states with well-defined orbital character, i.e. atomic-like electrons. The spectrum is typically dominated by d-electrons in transition metals, by f-electrons in the rare earths, and by s and p core states in the alkali and alkaline-earth metals. Figure 1 shows the orbital contributions to the Doppler broadening spectrum for copper. The spectrum at higher momentum values is dominated by the atomic-like d-electrons. These atomic-like orbitals have a momentum distribution that is determined primarily by their attraction to the nucleus, and so is little affected by solid-state effects. This suggests atomic calculations alone can provide accurate element-specific momentum densities at higher momentum without

requiring information about the atomic positions or performing complicated calculations for specific crystal or defect structures.

We have implemented a fast and reliable atomic-based procedure for calculating element-specific one-dimensional momentum distributions for comparison with coincidence Doppler-broadening measurements. A standard self-consistent-field atomic program [12] is used to compute the electron orbitals with an electronic configuration appropriate for the atom in the solid; for example, bulk copper should be calculated with a $(4s^13d^{10})$ valence electronic configuration. The positron potential is constructed using the self-consistent electron charge density from the atomic program and we solve for the unbound positron state around the atom at a fixed energy, typically chosen to be the energy zero for the atomic system. The electron and positron wavefunctions are then used to compute the electron-positron momentum density contribution from each electron orbital. This approach relies on the fact that the positron variation near the nucleus is essentially independent of the atomic environment, so the shape of the positron distribution and its relative overlap with the various core states for an atom in a solid is well represented in a purely atomic calculation.

The experimental spectrum contains the momentum density along one momentum direction corresponding to an integration of the three-dimensional momentum density over the other two directions in momentum space. In previous work [10,11], this one-dimensional momentum distribution was calculated from the spherically-symmetric three-dimensional radial momentum distribution around the atom by performing a two-dimensional integration in a cylindrical geometry. This approach involves an integral over momentum in the form

$$\rho(p_z) = \int_{p_z}^{\infty} p_r \rho_{3d}(p_r) dp_r$$

where p_r is the radial momentum, p_z is the one-dimensional momentum, and ρ_{3d} and ρ are the three-dimensional radial atomic momentum density and the 1-D momentum density respectively. This has the problem that it requires calculation of the radial momentum density to large momentum values. Although the momentum density becomes small at large values, it also begins to oscillate rapidly, leading to difficulties in convergence and the need for a finer radial grid for the real-space integrals involving the electron and positron wavefunctions. In order to avoid this problem we use an alternative formulation in which the integral over the two directions x and y in momentum space is performed analytically using the delta-function identity

$$\frac{1}{(2\pi)^2} \int e^{ip_{xy} \cdot r_{xy}} dp_{xy} = \delta(r_{xy}).$$

The resulting integrals for the one-dimensional momentum density are well-behaved real-space integrals, requiring an accuracy in integration comparable to that required for the atomic calculations. Full details will be presented elsewhere. This approach entirely avoids numerical p -space integration with the accompanying inaccuracies due to cutoffs in momentum space and rapidly-varying functions at high momentum. This approach is slower, since it requires an additional real-space integration for each radial grid point, but the method is still very fast and takes only a few seconds on a typical workstation.

This atomic-based method provides a fast and convenient way to calculate spectra without knowing the atomic positions, so it can be used for both amorphous and crystalline systems, and for defects with unknown defect geometries. The approach also has a number of limitations. First, the results are sensitive to the choice of electronic configuration for the atom, so the user is required to introduce assumptions about the electronic configuration. Fortunately this is not a severe approximation, since different reasonable choices result in spectra with similar features at the same positions in momentum. Second, the model does not account explicitly for environmental effects such as the changes in the shape of electron orbitals around a defect. These effects become less important at higher momentum, so it is reasonable to ignore them when we are most interested in the atom-specific high-momentum part of the spectrum. Third, this method does not give relative annihilation rates between different atomic species in multi-component systems. However, if this information is available from a solid-state-based positron calculation [13-16], the individual atomic spectra can be weighted by the relative annihilation rates to give a momentum density for a multi-component system. Finally, the results are sensitive to the treatment of the electron-positron enhancement factor [17], and a careful treatment of this enhancement is essential to produce physical results.

The electron-positron enhancement is treated using a generalized-gradient approximation [18,19]. In the atomic calculations, the charge density becomes vanishingly small at large distances from the nucleus. The density-functional-based electron-positron enhancement grows rapidly as the charge density becomes very small [17], resulting in a large enhancement of the more spatially-extended valence electrons and a corresponding increase in the low-momentum component of the spectrum. In the solid, the charge density never becomes as small as it does in atomic calculations, so the enhancement obtained from the atomic calculation will result in an unphysical enhancement for the more extended atomic orbitals in the solid. Two simple approaches are used to ensure that the treatment of enhancement in the atomic-based calculations is appropriate for solid-state systems. First, we truncate the radial integral at some cutoff radius. By imposing a cutoff of 3-4 a.u., the positron momentum density calculation is limited to the region where the atomic charge density is large enough to avoid unphysical enhancement. However the integral may miss a sizable fraction of the electron charge density with such a small cutoff, so in practice we choose a larger cutoff of around 10 a.u. With this cutoff, the charge density at large r is still small enough to result in an unphysically large enhancement on the valence electrons, so we impose a second correction by introducing a minimum charge density for the enhancement function. When the actual charge density is smaller than this minimum, the smaller enhancement factor associated with this minimum charge density is used. The choice of minimum charge density is determined by the system at hand. For example, in elemental metals it can be chosen to correspond to a physically meaningful density such as the interstitial charge density or the average conduction electron charge density. The resulting momentum densities are quantitatively affected by the choice of minimum charge density, but the resulting spectra are qualitatively very similar, as was the case for changes in the electronic configuration. In general the choice of a physically reasonable minimum charge density is straightforward and the resulting spectra are relatively insensitive to reasonable changes in its value.

We demonstrate the effectiveness of this method by comparing theoretical calculations with experiment for a number of systems. Figure 2 shows such a comparison for a number of elemental metals. In order to enhance the features in the otherwise rather featureless spectra, we have plotted the ratios of the momentum curves to a reference spectrum, in this case germanium. Note that neighboring elements such as Ni and Cu have rather similar spectra, while there are much clearer differences between these elements and Al. Figure 3 shows similar ratio spectra for a number of potassium halides. The observed experimental lineshapes correspond closely to the theoretical shapes of the associated halide. It is noteworthy that there is essentially no evidence for annihilation with the alkali metal atom in these spectra, and this has also been shown to be the case for a large number of alkali and alkaline-earth halides [20].

In the calculations presented here, we have made no attempt to improve agreement with experiment by varying the electronic configuration of the atom, the minimum charge density for the enhancement, or the energy of the positron. The general shapes of the ratio curves are relatively insensitive to changes in these parameters, and the calculations presented here are already accurate enough to allow discrimination between the various elements without requiring any further adjustment. We have investigated the changes in the calculated momentum densities with these parameters. The primary effect is to change to relative sensitivity to core and valence electrons; for example, increasing the positron energy leads to an increased positron overlap with the more tightly-bound core electrons, generally resulting in an increase in the momentum density at higher momentum values. These effects will be discussed in detail elsewhere.

In conclusion, we have demonstrated that an atomic-based program can produce theoretical one-dimensional momentum densities to aid in the interpretation of coincidence Doppler broadening spectra. The element-specific nature of the spectra at higher momentum values can be used to identify the nature of the electrons with which the positron is annihilating, and hence determine the atomic character of the region surrounding the positron in the solid. This atomic-based approach provides a fast and convenient way of identifying the “fingerprint” associated with a particular element in the Doppler-broadening spectrum.

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Figure Captions

1. Calculated electron-orbital decomposition of the 1-D electron-positron momentum density for Cu.
2. Experimental (a) and theoretical (b) coincidence Doppler ratio curves for a number of elemental metals. Experimental ratios are taken with respect to an experimental germanium spectrum. Theoretical ratios are taken with respect to a theoretical germanium spectrum, providing a more challenging test of the theory. The theoretical curves have been convoluted with a 0.38 a.u. gaussian to account for experimental resolution.
3. Experimental (a) and theoretical (b) coincidence Doppler spectra for a number of potassium halides. The correspondence of theory for the halides with experiment suggests that essentially all the annihilation is associated with the halide electrons.

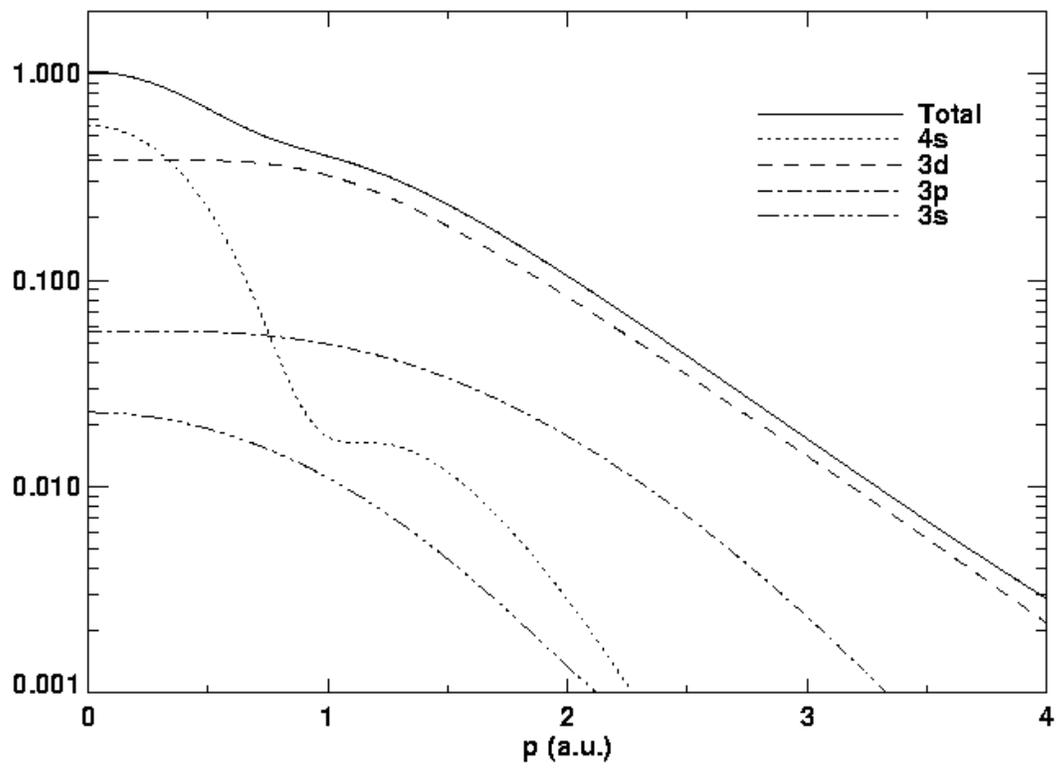


Fig.1

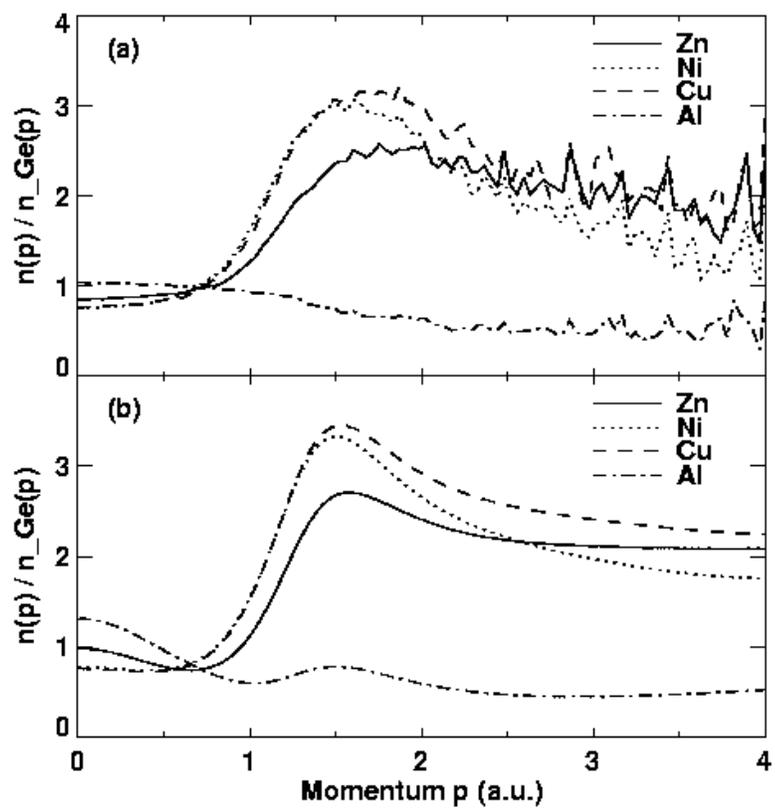


Fig. 2

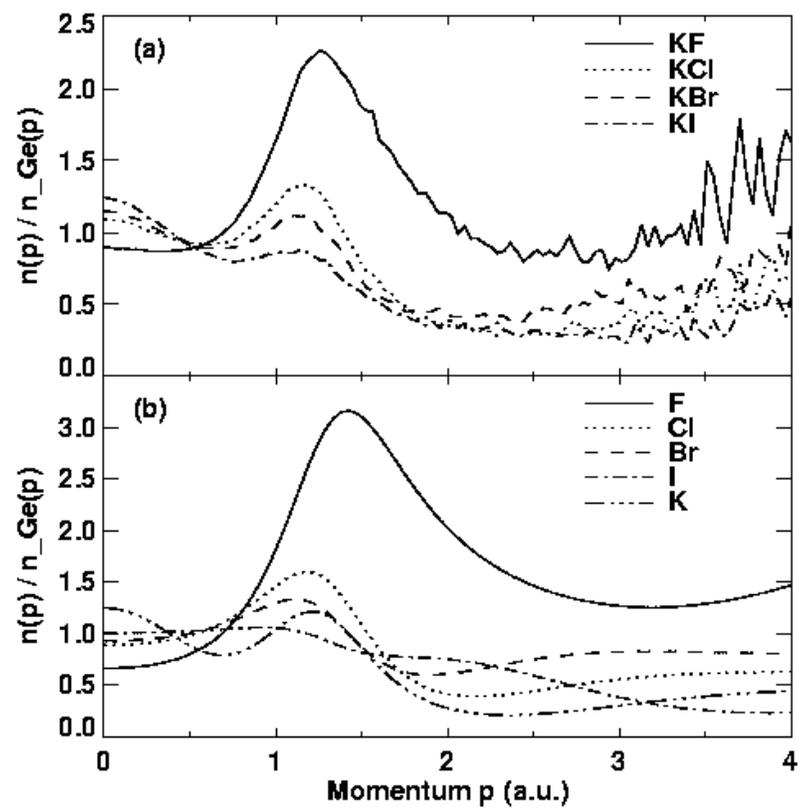


Fig. 3

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